



⑪ C CA No. 939876

④5 ISSUED Jan. 15, 1974

⑤2 CLASS 23-66
C.R. CL.

⑩ **CANADIAN PATENT**

⑤4 **PREPARATION OF PHOSPHATES**

Carlson, Ronald H., Lewiston, New York, U. S. A.

Granted to Hooker Chemical Corporation, Niagara Falls,
New York, U. S. A.

②1 APPLICATION No. 070, 327
②2 FILED Dec. 18, 1969

③0 PRIORITY DATE Dec. 30, 1968 (788, 095) U. S. A.

No. OF CLAIMS 4 - No drawing

10030263 040802

939876

The present invention relates to a process of preparing high-grade ammonium phosphates from crude wet process phosphoric acid. More particularly, the invention relates to a process for preparing solutions of ammonium phosphates substantially free from metal impurities by the acid-catalyzed thermal decomposition of urea in the presence of wet process phosphoric acid.

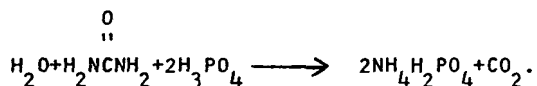
Ammonium phosphates are typically commercially produced by ammoniation of crude wet process phosphoric acid obtained from the acid decomposition of phosphate rocks, or other phosphate containing materials. The phosphate rock, such as fluorapatite, is acidulated with sulfuric acid, for example, and the calcium sulfate precipitate filtered off. The resulting phosphoric acid solution is then neutralized with ammonia to obtain the desired ammonium phosphate product. The phosphate rocks conventionally utilized as the source of phosphate contain significant amounts of metal impurities, which contaminate the wet process phosphoric acid obtained therefrom. Precipitation of these impurities, which include calcium, magnesium, manganese, and particularly iron and aluminum, is effected upon sufficient neutralization of the wet process phosphoric acid with ammonia. However, prior methods of neutralization with ammonia at atmospheric pressures have proved unsatisfactory, as the impurities present are thereby precipitated in a form which is not readily separable from the ammonium phosphate product. In particular, the iron and aluminum impurities are precipitated in a gelatinous form as complex iron-aluminum phosphates, which must be filtered from the desired ammonium phosphate product to render the product commercially acceptable. The filtration process is difficult, wasteful, and yields a low purity ammonium phosphate product.



939876

The present invention provides a simplified process for obtaining high purity ammonium phosphates from crude wet process phosphoric acid which obviates the use of complicated equipment such as pressure reactors and the involved processing techniques heretofore required.

According to the process of the present invention, a solution of crude, wet process phosphoric acid containing wet acid impurities and urea, or a hydrolyzable urea derivative, is prepared, and the solution heated until precipitation of the wet acid impurities occurs. The urea is hydrolyzed to form ammonia and carbon dioxide, the former reacting with the phosphoric acid to form ammonium phosphates while the latter is evolved. The reaction may be represented by the following general equation.



Although the product is represented above as monoammonium phosphate, infrared analysis confirms that the product is actually a mixture of the mono- and di- ammonium phosphates.

The process, by generating ammonia in situ, permits the homogenous, in place precipitation of the wet acid impurities in a particle size that enables the precipitate to be readily separated from the ammonium phosphate product. Urea is preferred as the source of ammonia, although hydrolyzable urea derivatives may be effectively substituted. Up to about stoichiometric amounts of the reactants may be employed, while a molar ratio of urea to phosphoric acid of from about 1 to 2 to about 1 to 1 is preferred. Utilizing less urea results in inadequate neutralization of the phosphoric acid solution, while an excess of urea, although not necessarily detrimental to the reaction, is superfluous. The reaction is conducted at atmospheric pressure, at reflux temperatures for example of about

939876

95-105 degrees centigrade. The reaction is continued until precipitation of the wet acid impurities is achieved, a period of about 24 hours, although the time required to complete the reaction may vary depending on the particular chemical make-up of the crude phosphoric acid solution employed. At termination of the reaction the precipitate is separated from the solution, preferably by filtration, or by other known methods. The filter cake, containing ammonium phosphate and the wet acid impurities, is commonly washed, and the wash solution added to the filtrate; this solution may be further processed by decolorization with charcoal.

The ammonium phosphates obtained are particularly valuable for use in the production of fertilizers. The high purity ammonium phosphate solutions obtained by the method of this invention are especially advantageously used in liquid fertilizer formulations. However, if desired, solid ammonium phosphates suitable for use in solid fertilizers may be recovered from the ammonium phosphate solutions. This may be readily accomplished by concentrating the filtrate obtained from the reaction mixture by heating, followed by rapid cooling of the solution, and separation of the resultant solid ammonium phosphates from the solution.

The following examples will serve to illustrate the process of the present invention:

EXAMPLE 1

Preparation of a clear liquid ammonium phosphate solution:
To 50.4g (0.83 mole) of urea dissolved in 100 ml. of distilled water was added with stirring 130g. (1.0 mole H_3PO_4) of crude wet process phosphoric acid (analysis: 54.6% P_2O_5 , 4.95% SO_4^{-2} , 1.41% Fe_2O_3 , 1.23% Al_2O_3 , 0.42% F). The resulting solution was refluxed for twenty-four hours at a temperature of 103-104 degrees centigrade.

939876

The pH of the reaction mixture gradually rose during reflux, indicating urea hydrolysis to be taking place. At termination of reflux, an olive green slurry of pH 5.81 (79 degrees centigrade) was present; this material was filtered hot on a 5.5 cm. Buchner funnel fitted with a Dacron cloth. A good filter rate of 810 grams of slurry/min.-100 cm² filter area was obtained. (This filter rate is to be compared with rates of 10-20g./min.-100 cm² obtained by direct ammoniation of wet-process acid to a comparable pH level with no special precautions taken to insure good filterability.) The filter cake was washed with 86 ml. of distilled water and the combined filtrate and wash solution treated with activated charcoal with heating to yield on filtration a clear, pale-green ammonium phosphate solution of pH 6.0, which analyzed for: 6.21% N, 18.2% P₂O₅, 141 ppm Fe, 30 ppm Al. Infrared spectra of this solution confirmed a mixture of diammonium and monoammonium phosphate. A solution of this type could readily fit into the liquid fertilizer market.

EXAMPLE 2

A crude wet phosphoric acid solution of composition similar to that in Example 1 was subjected to direct ammoniation by the introduction of gaseous ammonia until a pH of 6.0 was reached; reaction temperature reached 90 degrees centigrade during the ammoniation. The reaction mixture was filtered according to Example 1. A filter rate of 20g./min-100 cm² was obtained.

939876

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

- 1 -

A process for the production of high purity ammonium phosphate from crude wet-process phosphoric acid, which process comprises

(a) reacting crude wet-process phosphoric acid containing impurities with urea, said phosphoric acid present in an amount of from about stoichiometric amounts to about 2:1 with said urea, said reaction conducted at a temperature of from about 95°C to about 150°C at atmospheric pressures for a period of time sufficient to precipitate said impurities from the reaction mixture as a readily filterable precipitate;

(b) separating the precipitated impurities; and

(c) recovering high purity ammonium phosphate.

- 2 -

A process for the production of high purity ammonium phosphate from crude wet-process phosphoric acid containing iron and aluminum impurities, which process comprises

(a) reacting at a temperature of from about 95°C to about 105°C at atmospheric pressures and at a pH of from about 5.8 to about 6.0, crude wet-process phosphoric acid with urea in amounts sufficient to provide a molar ratio of phosphoric acid to urea of about 2:1 to 1:1, based on the amide functionality of said urea, said reaction conducted for a period of time sufficient to precipitate said iron and aluminum impurities as a readily filterable precipitate,

(b) separating the precipitated impurities; and

(c) recovering high purity ammonium phosphate.

- 3 -

A process as defined by Claim 1 wherein the reaction is conducted for a period of from about 12 to about 24 hours.

- 4 -

A process as defined by Claim 2 wherein the reaction is conducted for a period of from about 12 to about 24 hours.

B

5

